PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C11D 1/825	A1	(11) International Publicati n Number: **WO 00/50552** (43) Internati nal Publication Date: 31 August 2000 (31.08.00)

(21) International Application Number: PCT/US00/03454

(22) International Filing Date: 10 February 2000 (10.02.00)

(30) Priority Data:
60/121,174 22 February 1999 (22.02.99) US

(71) Applicant (*for all designated States except US*): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): HAGGEBERG, Donna, Jean [US/US]; 2067 Greenpin Drive, Cincinnati, OH 45231 (US). SCHEPER, William, Michael [US/US]; 2393 Picnic Woods Drive, Lawrenceburg, IN 47025 (US). JORDAN, Glenn, Thomas, IV [US/US]; 5750 Ridgeview Drive, Indian Springs, OH 45011 (US).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD OF REMOVING STAINS FROM A SURFACE

(57) Abstract

A method for removing stains from a hydrophobic surface such as plastic, including the steps of applying an aqueous solution of a composition which comprises: (a) from 0.1% to 15% by weight of the composition of an amine oxide, phosphine oxide, sulfoxide or mixtures thereof; (b) from 0.1% to 15% by weight of the composition of one or more low cloud point nonionic surfactants having a cloud point of less than 30 °C, selected from ethoxylated-propoxylated alcohol, capped poly(oxyalkylated) alcohols and mixtures thereof, wherein said capped nonionic surfactant is substantially free of dimers and trimers; (c) optionally, an oxygen bleaching agent; (d) optionally, a builder; and (e) adjunct materials, preferably automatic dishwashing detergent adjunct materials selected from the group consisting of enzymes, chelating agents, and mixtures thereof; wherein the weight ratio the nonionic surfactants to the oxide surfactant is within the range of from 25:1 to 1:5; the stains are selected from tomato stains, carotene stains, and mixtures thereof; and wherein the composition prevents redeposition of the stains once it has been removed from the stained surface.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

METHOD OF REMOVING STAINS FROM A SURFACE

TECHNICAL FIELD

The present invention relates to methods of removing stains from a surface using a composition containing a specific combination of surfactants. Preferred compositions used are automatic dishwashing detergent compositions containing an oxygen bleaching systems, further preferably comprising bleach activators and/or metal-containing bleach catalysts (e.g., manganese and/or selected cobalt/ammonia catalysts), and detersive enzymes (e.g., amylase; protease).

BACKGROUND OF THE INVENTION

In household cleaning formulation, such as hard surface cleaning compositions (HSC) and automatic dishwashing compositions (ADW), the problem of "red sauce redeposition" is well know. This is when a surface is cleaned, such as in an automatic dishwasher, and the soil redeposits back on to a surface that has just been cleaned, leaving the surface stained and unsightly. Once the stain has dried it effectively is a permanent addition to the surface, and virtually impossible to remove. This is especially true of hydrophobic surfaces, for example plastic. Numerous attempts have been made to deal with this deposition. This "red sauce redeposition" is caused by soils which contain tomato soils, such as lasagna, carotene soils, such as in cooked carrots, (also known as lycopene soils) and mixtures thereof.

One solution which has been attempted is the use of bleaches, to prevent the formation of the "red soil" stains and remove existing ones. However, the bleaches have a minimal effect on the existing stains and preventing the formation of more "red soil" stains. Furthermore, some bleaches while cleaning the surface better, only exacerbate the problem by removing more soil which is then more able to redeposit on to the surfaces to for "red sauce redeposition".

Consequently, there remains the need for a way to prevent the formation of this "red sauce redeposition" by preventing the redeposition on to a surface of the "red soil".

BACKGROUND ART

WO 94/22800, published October 13, 1994 by Olin Corporation, US Serial No. 08/763,997 Filed December 12, 1996, .

SUMMARY OF THE INVENTION

It has now been surprisingly found that that methods using compositions comprising an oxide surfactant and specific nonionic surfactants prevent the redeposition of "red soil", and thereby preventing "red sauce redeposition" from occurring. This is surprising considering that oxide surfactant surfactants, such as amine oxide, are high sudsing surfactants making them unsuitable for use in situations which require low foam, such as in automatic dishwashing

applications. It is this specific combination of oxide surfactant and specific nonionic surfactants in compositions which prevents the formation of "red sauce redeposition".

The present invention therefore encompasses a method for removing stains from a surface and preventing the redeposition of soil from a surface comprising the steps of applying an aqueous solution of a composition to a stained surface in need of stain removal, wherein the composition comprises:

(a) from about 0.1% to about 15%, preferably from about 0.2% to about 10%, more preferably from about 0.5% to about 5%, weight of the composition of an oxide surfactant, the oxide surfactant being selected from the group consisting of, amine oxides, phosphine oxides, sulfoxides and mixtures thereof;

(b) from about 0.1% to about 15%, preferably from about 0.2% to about 10%, more preferably from about 0.5% to about 5%, by weight of the composition of one or more low cloud point nonionic surfactants having a cloud point of less than 30°C the nonionic surfactants are selected from the group consisting of ethoxylated-propoxylated alcohol, capped poly(oxyalkylated) alcohols and mixtures thereof, wherein said capped nonionic surfactant is substantially free of dimers and trimers;

(c) optionally, from about 0.1% to about 40% by weight of the composition of an oxygen bleaching agent;

(d) optionally, from about 5% to about 90%, preferably from about 5% to about 75%, more preferably from about 10% to about 50% by weight of the composition of a builder; and

(e) adjunct materials, preferably automatic dishwashing detergent adjunct materials selected from the group consisting of enzymes, chelating agents, and mixtures thereof;

wherein the weight ratio the nonionic surfactants to the oxide surfactant being within the range of from about 25:1 to about 1:5, preferably about 3:1 to about 15:1; the stained surface is a hydrophobic surface; the stains are selected from the group consisting of tomato stains, carotene stains, and mixtures thereof; and wherein the composition prevents redeposition of the stains once it has been removed from the stained surface.

The preferred compositions useful in the methods herein comprise a bleaching system which is a source of hydrogen peroxide, preferably perborate and/or percarbonate, and preferably also comprise a cobalt-containing bleach catalyst or a manganese-containing bleach catalyst. Preferred cobalt-containing bleach catalysts have the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\,T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 M^{-1} s^{-1} (25°C). Also, in another mode, the compositions useful in the methods of the present invention are those wherein the bleach catalyst is a member selected from the group consisting of manganese bleach catalysts, especially manganese "TACN", as described more fully hereinafter.

Additional bleach-improving materials can be present such as bleach activator materials, including tetraacetylethylenediamine ("TAED") and cationic bleach activators, e.g., 6-trimethylammoniocaproyl caprolactam, tosylate salt.

The preferred compositions useful in the methods herein further comprise a protease and/or amylase enzyme. Whereas conventional amylases such as TERMAMYL® may be used with excellent results. Preferred compositions can use oxidative stability-enhanced amylases. Such an amylase is available from Novo Nordisk (described more fully in WO 94/02597, published February 3, 1994) and from Genencor International (described more fully in WO 94/18314, published August 18, 1994) Oxidative stability is enhanced by substitution of the methionine residue located in position 197 of B.Licheniformis or the homologous position variation of a similar parent amylase. Typical proteases include Esperase, Savinase, and other proteases as described hereinafter.

The present invention encompasses (but is not limited to) the use of granular-form, fully-formulated automatic dishwashing compositions in which additional ingredients, including other enzymes (especially proteases and/or amylases) are formulated.

All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

Method of the present invention

It is preferred that the method of the present invention be performed in an automatic dishwasher, with the composition used being an ADW composition. However, the composition could also be a HSC composition and the method could be performed on a hydrophobic surface like a plastic cutting board, on a vinyl floor or on a kitchen counter top.

It is preferred that after the composition is applied to the stained surface that the surface is rinsed with water, more preferably, rinsed twice.

Stains

The stains which the method of the present invention seek to remove and prevent redeposition are selected from tomato satins, carotene stains (also know as lycopene stains) and mixtures thereof. These soils are well know in the art to cause the "red soil redeposition" which causes the unsightly staining of hydrophobic surfaces.

Hydrophobic surface

Hydrophobic surfaces mean any surface which naturally repels water. The best example of this is plastic. In the method of the present invention the hydrophobic surface is defined as any hydrophobic surface which could suffer "red sauce redeposition" during cleaning. This would mean that if the method was performed in an automatic dishwasher, then any possible hydrophobic surface in the automatic dishwasher is meant. This would include not only those which are put in the dishwasher to be cleaned, such as plasticware, tableware, plates, knives, forks, spoons, cookware, ladles, spatulas, spoons, baby bottle, baby pacifies, and other infant feeding equipment, but also any of the internal surfaces of the automatic dishwasher itself, such as the dish racks, silverware racks, the sprayer arm, or even the internal walls of the dishwasher. Plastics, would include, but are not limited to, acrylates, methacrylates, high density polyethylene, PET, POET, PVC, melanine, and copolymers of these.

Compositions used in the method of the present invention

The compositions used in the present invention may be in any suitable form, such as a liquid, granule, powder, tablet, liqui-gel, gel, thixatropic liquid. It is preferred that the compositions used in the methods of the present invention be in the form of automatic dishwashing compositions (ADD). However, other compositions, such as hard surface cleaning compositions (HSC), can be used in the methods of the present invention.

The compositions used in the methods of the present invention comprise a mixed surfactant system, and preferably also include builder, bleaching agent (such as a source of hydrogen peroxide) and/or detersive enzymes. Bleaching agents useful herein include sources of hydrogen peroxide, including any common hydrogen-peroxide releasing salt, such as sodium perborate, sodium percarbonate, and mixtures thereof. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). In the preferred embodiments, additional ingredients such as water-soluble silicates (useful to provide alkalinity and assist in controlling corrosion), dispersant polymers (which modify and inhibit crystal growth of calcium and/or magnesium salts), chelants (which control transition metals), alkalis (to adjust pH), and detersive enzymes (to assist with tough food cleaning, especially of starchy and proteinaceous soils), are present. Additional bleach-modifying materials such as conventional bleach activators (e.g. TAED and/or bleach catalysts) may be added, provided that any such bleach-modifying materials are delivered in such a manner as to be compatible with the purposes of the present invention. The present useful compositions may, moreover, comprise

one or more processing aids, fillers, perfumes, conventional enzyme particle-making materials including enzyme cores or "nonpareils", as well as pigments, and the like.

In general, materials used for the production of the compositions used herein are preferably checked for compatibility with spotting/filming on glassware. Test methods for spotting/filming are generally described in the automatic dishwashing detergent literature, including DIN and ASTM test methods. Certain oily materials, especially at longer chain lengths, and insoluble materials such as clays, as well as long-chain fatty acids or soaps which form soap scum are therefore preferably limited or excluded from the instant compositions.

Amounts of the essential ingredients can vary within wide ranges, however preferred automatic dishwashing detergent compositions herein (which typically have a 1% aqueous solution pH of above about 8, more preferably from about 9.5 to about 12, most preferably from about 9.5 to about 10.5) are those wherein there is present: from about 5% to about 90%, preferably from about 5% to about 75%, of builder; from about 0.1% to about 40%, preferably from about 0.5% to about 30%, of bleaching agent; from about 0.1% to about 15%, preferably from about 0.2% to about 10%, of the mixed surfactant system; from about 0.0001% to about 1%, preferably from about 0.001% to about 0.05%, of a metal-containing bleach catalyst (most preferred cobalt catalysts useful herein are present at from about 0.001% to about 0.01%); and from about 0.1% to about 40%, preferably from about 0.1% to about 20% of a water-soluble (two ratio) silicate. Such fully-formulated embodiments typically further comprise from about 0.1% to about 15% of a polymeric dispersant, from about 0.01% to about 10% of a chelant, and from about 0.00001% to about 10% of a detersive enzyme, though further additional or adjunct ingredients may be present. The compositions used herein in granular form typically limit water content, for example to less than about 7% free water, for best storage stability.

While the compositions useful in the methods of this invention (especially those comprising detersive enzymes) are substantially free of chlorine bleach. By "substantially free" of chlorine bleach is meant that the formulator does not deliberately add a chlorine-containing bleach additive, such as a dichloroisocyanurate, to the composition to be used. However, it is recognized that because of factors outside the control of the formulator, such as chlorination of the water supply, some non-zero amount of chlorine bleach may be present in the wash liquor. The term "substantially free" can be similarly constructed with reference to preferred limitation of other ingredients.

By "effective amount" herein is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance cleaning of a soiled surface. Likewise, the term "catalytically effective amount" refers to an amount of metal-containing bleach catalyst which is sufficient under whatever comparative test conditions are employed, to enhance cleaning of the soiled surface. In automatic dishwashing, the soiled surface may be, for

example, a porcelain cup with tea stain, a porcelain cup with lipstick stain, dishes soiled with simple starches or more complex food soils, or a plastic spatula stained with tomato soup. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some machines have considerably longer wash cycles than others. Some users elect to use warm water without a great deal of heating inside the appliance; others use warm or even cold water fill, followed by a warm-up through a built-in electrical coil. Of course, the performance of bleaches and enzymes will be affected by such considerations, and the levels used in fully-formulated detergent and cleaning compositions can be appropriately adjusted.

Surfactant System

Surfactants useful in the method of the present invention are desirably included in the present detergent compositions at levels of from about 0.1% to about 15% of the composition. In general, bleach-stable surfactants are preferred. The surfactant system used may include optional surfactants such as other nonionic surfactants, such as high cloud point surfactants, anionic surfactants, such as alkylethoxysulfates, zwitterionic surfactants, such as betaines, and mixtures thereof.

The essential surfactant system useful herein are mixtures of a low cloud point nonionic surfactant combined with an oxide surfactant in a weight ratio preferably within the range of from about 25:1 to about 1:5, preferably from about ??? to about ???, more preferably from about 3:1 to about 15:1.

Oxide Surfactant - The oxide surfactant is selected from the group consisting of, amine oxides, phosphine oxides, sulfoxides and mixtures thereof, with amine oxide being preferred.

Preferred amine oxides have the formula

$$R^3(OR^4)_x\overset{\overset{\displaystyle O}{|}}{N}(R^5)_2$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups.

Preferred phosphine oxides have the formula

$$R^3(OR^4)_x\overset{\overset{\displaystyle O}{|}}{P}(R^5)_2$$

wherein R^3, R^4, x, and R^5 are as herein before defined.

Preferred sulfoxides have the formula

$$R^3(OR^4)_x\overset{\overset{\displaystyle O}{|}}{S}(R^5)_2$$

wherein R^3, R^4, x, and R^5 are as herein before defined.

Essential nonionic surfactant - The one or more low cloud point nonionic surfactants having a cloud point of less than 30°C, are selected from the group consisting of ethoxylated-propoxylated alcohol, capped poly(oxyalkylated) alcohols and mixtures thereof; wherein the capped nonionic surfactant is substantially free of dimers and trimers. Examples of suitable surfactants are ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF-18) and epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF-18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation).

As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than about 20°C, and more preferably less than about 10°C.

It is also preferred for purposes of the present invention that the low cloud point nonionic surfactant further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from about 1 to about 10, preferably 3 to 8. Such materials include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF-18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF-18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation), REVERSED PLURONIC® 25R2 and TETRONIC® 702.

Optional nonionic surfactant - The optional nonionic surfactant may be a low cloud point nonionic other than the essential low cloud point nonionics, high cloud point nonionics and mixtures thereof, with high cloud point being preferred.

Nonionic surfactants generally are well known, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detersive Systems", incorporated by reference herein. While a wide range of nonionic surfactants may be selected from for purposes of the mixed surfactant systems useful in the present invention ADD compositions, it is necessary that the surfactant system comprise both a low cloud point nonionic surfactant(s) and a charged surfactant as described as follows. "Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer, pp. 360-362, hereinbefore).

Typical low cloud point nonionic surfactants include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers.

Nonionic surfactants can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Low cloud point nonionic surfactants additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC® 25R2 and TETRONIC® 702, Such surfactants are typically useful herein as low cloud point nonionic surfactants.

As used herein, a "high cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of greater than 40°C, preferably greater than about 50°C, and more preferably greater than about 60°C. Preferably the nonionic surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

It is also preferred for purposes of the present invention that such high cloud point nonionic surfactants further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from about 9 to about 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from about 6 to about 20 carbon atoms (C_6-C_{20} alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/11 or C11/15 branched alcohol ethoxylates, condensed with an average of from about 6 to about 15 moles, preferably from about 6 to about 12 moles, and most preferably from about 6 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

Finally, if a high cloud point nonionic surfactant is also used, preferred ratios of high cloud point nonionic surfactant to the oxide surfactant are within the range of from about 1:2 to 10:1, preferably 1:1 to 4:1, and it is further to be recognized that the ratio of low cloud point nonionic surfactant to the combination of oxide surfactant and high cloud point nonionic surfactant is within the range of from about 20:1 to about 1:5. It is preferred to use ADD compositions comprising such mixed surfactant systems wherein the sudsing (absent any silicone suds controlling agent) is less than 2 inches, preferably less than 1 inch, determined as follows.

Optional Anionic surfactant - While it is not preferred it is possible to include in the compositions used in the methods of the present invention an anionic surfactant. When the composition to be used is an ADD, the anionic surfactant is chosen from alkylethoxycarboxylates, alkylethoxysulfates, with the degree of ethoxylation greater than 3 (preferably 4 to 10; more preferably 6 to 8), and chain length in the range of C8 to C16, preferably 11-15. Additionally, branched alkylcarboxylates have been found to be useful for the purpose of the present invention when the branch occurs in the middle and the average total chain length is 10 to 18, preferably 12-16 with the side branch 2-4 carbons in length. An example is 2-butyloctanoic acid. The anionic surfactant is typically of a type having good solubility in the presence of calcium. Such anionic surfactants are further illustrated by sulfobetaines, alkyl(polyethoxy)sulfates (AES), alkyl (polyethoxy)carboxylates (AEC), and short chained C_6-C_{10} alkyl sulfates and sulfonates. Straight chain fatty acids have been shown to be ineffective due to their sensitivity to calcium.

Measuring Dishwasher Arm RPM Efficiency and Wash Suds Height:

The equipment useful for these measurements are: a Whirlpool Dishwasher (model 900) equipped with clear plexiglass door, IBM computer data collection with Labview and Excel Software, proximity sensor (Newark Corp. - model 95F5203) using SCXI interface, and a plastic ruler.

The data is collected as follows. The proximity sensor is affixed to the bottom dishwasher rack on a metal bracket. The sensor faces downward toward the rotating dishwasher arm on the bottom of the machine (distance approximately 2 cm. from the rotating arm). Each pass of the rotating arm is measured by the proximity sensor and recorded. The pulses recorded by the computer are converted to rotations per minute (RPM) of the bottom arm by counting pulses over a 30 second interval. The rate of the arm rotation is directly proportional to the amount of suds in the machine and in the dishwasher pump (i.e., the more suds produced, the slower the arm rotation).

The plastic ruler is clipped to the bottom rack of the dishwasher and extends to the floor of the machine. At the end of the wash cycle, the height of the suds is measured using the plastic ruler (viewed through the clear door) and recorded as suds height.

The following procedure is followed for evaluating ADD compositions for suds production as well as for evaluating nonionic surfactant systems for utility in such systems. (For separate evaluation of nonionic surfactant systems, a base ADD formula, such as Cascade powder, is used along with the nonionic surfactants which are added separately in glass vials to the dishwashing machine.)

First, the machine is filled with water (adjust water for appropriate temperature and hardness) and proceed through a rinse cycle. The RPM is monitored throughout the cycle (approximately 2 min.) without any ADD product (or sufactants) being added (a quality control check to ensure the machine is functioning properly). As the machine begins to fill for the wash cycle, the water is again adjusted for temperature and hardness, and then the ADD product is added to the bottom of the machine (in the case of separately evaluated surfactant systems, the ADD base formula is first added to the bottom of the machine then the surfactants are added by placing the surfactant-containing glass vials inverted on the top rack of the machine). The RPM is then monitored throughout the wash cycle. At the end of the wash cycle, the suds height is recorded using the plastic ruler. The machine is again filled with water (adjust water for appropriate temperature and hardness) and runs through another rinse cycle. The RPM is monitored throughout this cycle.

An average RPM is calculated for the 1st rinse, main wash, and final rinse. The %RPM efficiency is then calculated by dividing the average RPM for the test surfactants into the average RPM for the control system (base ADD formulation without the nonionic surfactant system). The RPM efficiency and suds height measurements are used to dimension the overall suds profile of the surfactant system.

Builders

Detergent builders other than silicates can optionally be included in the compositions used herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are used in automatic dishwashing to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. The compositions will typically comprise at least about 1% builder. High performance compositions typically comprise from about 5% to about 90%, more typically from about 5% to about 75% by weight, of the detergent builder. Lower or higher levels of builder, however, are not excluded.

Inorganic or non-phosphate-containing detergent builders include, but are not limited to, phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulfates, citrate, zeolite or layered silicate, and aluminosilicates.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Various grades and types of sodium carbonate and sodium sesquicarbonate may be used, certain of which are particularly useful as carriers for other ingredients, especially detersive surfactants.

Aluminosilicate builders may be used in the present compositions though are not preferred for automatic dishwashing detergents. (See U.S. Pat. 4,605,509 for examples of preferred aluminosilicates.) Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula: $Na_2O \cdot Al_2O_3 \cdot xSiO_z \cdot yH_2O$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In another embodiment, the crystalline aluminosilicate ion exchange material has the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$ wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. Individual particles can desirably be even smaller than 0.1 micron to further assist kinetics of exchange through maximization of surface area. High surface area also increases utility of aluminosilicates as adsorbents for surfactants, especially in granular compositions. Aggregates of silicate or aluminosilicate particles may be useful, a single aggregate having dimensions tailored to minimize segregation in granular compositions, while the aggregate particle remains dispersible to submicron individual particles during the wash. As with other builders such as carbonates, it may be desirable to use zeolites in any physical or morphological form adapted to promote surfactant carrier function, and appropriate particle sizes may be freely selected by the formulator.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein,

"polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt or "overbased". When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediaminetetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty laundry detergent and automatic dishwashing formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in combination with zeolite, the aforementioned BRITESIL types, and/or layered silicate builders. Oxydisuccinates are also useful in such compositions and combinations.

Also suitable in the compositions used in the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedionates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, may also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity but are generally not desired. Such use of fatty acids will generally result in a diminution of sudsing in laundry compositions, which may need to be taken into account by the formulator. Fatty acids or their salts are undesirable in Automatic Dishwashing (ADD) embodiments in situations wherein soap scums can form and be deposited on dishware.

Where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used though such materials are more commonly used in a low-level mode as chelants or stabilizers.

Phosphate detergent builders for use in ADD compositions are well known. They include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates). Phosphate builder sources are described in detail in Kirk Othmer, 3rd Edition, Vol. 17, pp. 426-472 and in "Advanced Inorganic Chemistry" by Cotton and Wilkinson, pp. 394-400 (John Wiley and Sons, Inc.; 1972).

Preferred levels of phosphate builders herein are from about 5% to about 90%, preferably from about 5% to about 75%, more preferably from about 10% to about 50% by weight of phosphate builder.

Bleaching Agents

Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms. An "effective amount" of a source of hydrogen peroxide is any amount capable of measurably improving stain removal (especially of tea stains) from soiled dishware compared to a hydrogen peroxide source-free composition when the soiled dishware is washed by the consumer in a domestic automatic dishwasher in the presence of alkali.

More generally a source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen

peroxide. Levels may vary widely and are usually in the range from about 0.1% to about 70%, more typically from about 0.5% to about 30%, by weight of the compositions used herein.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

While effective compositions useful herein may comprise only the mixed surfactant system and builder, useful fully-formulated compositions typically will also comprise other adjunct materials to improve or modify performance. These materials are selected as appropriate for the properties required of composition. For example, low spotting and filming is desired -- preferred compositions have spotting and filming grades of 3 or less, preferably less than 2, and most preferably less than 1, as measured by the standard test of The American Society for Testing and Materials ("ASTM") D3556-85 (Reapproved 1989) "Standard Test Method for Deposition on Glassware During Mechanical Dishwashing".

Adjunct Materials:

The compositions used in the methods of the present invention contain an adjunct material. It is preferred that the adjunct material be an ADD adjunct material, as the preferred form of the compositions used is as an ADD composition.

Detersive ingredients or adjuncts optionally included in the compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. They are further selected based on the form of the composition, i.e., whether the composition is to be sold as a liquid, paste (semi-solid), or solid form (including tablets and the preferred granular forms for the present compositions). Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total, from about 30% to about 99.9%, preferably from about 70% to

about 95%, by weight of the compositions), include other active ingredients such as non-phosphate builders, chelants, enzymes, suds suppressors, dispersant polymers (e.g., from BASF Corp. or Rohm & Haas), color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, dyes, fillers, germicides, alkalinity sources, hydrotropes, anti-oxidants, enzyme stabilizing agents, perfumes, solubilizing agents, carriers, processing aids, pigments, pH control agents, and, for liquid formulations, solvents, as described in detail hereinafter.

1. Detersive Enzymes

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more bleach compatible, have a remaining degree of bleach deactivation susceptibility.

In general, as noted, preferred compositions used herein comprise one or more detersive enzymes. If only one enzyme is used, it is preferably an amyolytic enzyme when the composition is for automatic dishwashing use. Highly preferred for automatic dishwashing compositions is a mixture of proteolytic enzymes and amyloytic enzymes. More generally, the enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders, etc. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated in the compositions used herein at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal or soil removal effect on substrates such as fabrics, dishware and the like. Since enzymes are catalytic materials, such amounts may be very small. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 6%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For automatic dishwashing purposes, it may be desirable to increase the active enzyme content of the commercial preparations, in order to minimize the total amount of non-catalytically active materials delivered and thereby improve spotting/filming results.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S as ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

An especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Amylases suitable herein include, for example, α-amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo Industries.

Engineering of enzymes (e.g., stability-enhanced amylase) for improved stability, e.g., oxidative stability is known. See, for example J.Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. "Reference amylase" refers to a conventional amylase inside the scope of the amylase component of this invention. Further, stability-enhanced amylases, also within the invention, are typically compared to these "reference amylases".

The present invention, in certain preferred embodiments, can makes use of amylases having improved stability in detergents, especially improved oxidative stability. A convenient absolute stability reference-point against which amylases used in these preferred embodiments of the instant invention represent a measurable improvement is the stability of TERMAMYL®

in commercial use in 1993 and available from Novo Nordisk A/S. This TERMAMYL® amylase is a "reference amylase", and is itself well-suited for use in the ADD (Automatic Dishwashing Detergent) compositions of the invention. Even more preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, all measured versus the above-identified reference-amylase. Preferred amylases herein can demonstrate further improvement versus more challenging reference amylases, the latter reference amylases being illustrated by any of the precursor amylases of which preferred amylases within the invention are variants. Such precursor amylases may themselves be natural or be the product of genetic engineering. Stability can be measured using any of the art-disclosed technical tests. See references disclosed in WO 94/02597, itself and documents therein referred to being incorporated by reference.

In general, stability-enhanced amylases respecting the preferred embodiments of the invention can be obtained from Novo Nordisk A/S, or from Genencor International.

Preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the Baccillus amylases, especialy the Bacillus alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

As noted, "oxidative stability-enhanced" amylases are preferred for use herein despite the fact that the invention makes them "optional but preferred" materials rather than essential. Such amylases are non-limitingly illustrated by the following:

(a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the B.licheniformis alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as B. amyloliquefaciens, B.subtilis, or B.stearothermophilus;

(b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from B.licheniformis NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8,15,197,256,304,366 and 438 leading to specific mutants, particularly

important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®;

(c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S. These amylases do not yet have a tradename but are those referred to by the supplier as QL37+M197T.

Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases.

Cellulases usable in, but not preferred, for the present invention include both bacterial or fungal cellulases. Typically, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful.

Suitable lipase enzymes for detergent use include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE® enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein. Another preferred lipase enzyme is the D96L variant of the native Humicola lanuginosa lipase, as described in WO 92/05249 and Research Disclosure No. 35944, March 10, 1994, both published by Novo. In general, lipolytic enzymes are less preferred than amylases and/or proteases for automatic dishwashing embodiments of the present invention.

Peroxidase enzymes can be used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-

peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. The present invention encompasses peroxidase-free automatic dishwashing composition embodiments.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

2. Enzyme Stabilizing System - The enzyme-containing compositions, especially liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, and mixtures thereof.

The stabilizing system of the compositions used herein may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is relatively large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely known and readily available, and are illustrated by salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by several of the ingredients separately listed under better recognized functions, (e.g., other

components of the invention such as sodium perborate), there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any scavenger which is majorly incompatible with other ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in U.S. Patent 4,652,392, Baginski et al.

3. Optional Bleach Adjuncts

(a) Bleach Activators -

Preferably, the peroxygen bleach component in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzene-sulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C_{10}-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and 4,412,934, Chung et al, and copending patent applications U. S. Serial Nos. 08/064,624, 08/064,623, 08/064,621, 08/064,562, 08/064,564, 08/082,270 and copending application to M. Burns, A. D. Willey, R. T. Hartshorn, C. K. Ghosh, entitled "Bleaching Compounds Comprising Peroxyacid Activators Used With Enzymes" and having U.S. Serial No. 08/133,691 (P&G Case 4890R), all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 3:1.

Quaternary substituted bleach activators may also be included. The present detergent compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in copending U.S. Serial No. 08/298,903, 08/298,650, 08/298,906 and 08/298,904 filed August 31, 1994, incorporated herein by reference.

(b) Organic Peroxides, especially Diacyl Peroxides - These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

(c) Metal-containing Bleach Catalysts:

The present invention methods may optionally utilize metal-containing bleach catalysts that are effective for use in ADD compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of theses catalysts include $Mn^{IV}_2(u\text{-}O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(PF_6)_2$ ("MnTACN"), $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6(1,4,7\text{-triazacyclononane})_4\text{-}(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(ClO_4)_3$, and mixtures thereof. See also European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful in automatic dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084.

See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $Mn(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}(OCH_3)_3\text{-}(PF_6)$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulsitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:

$$\begin{array}{ccccccccc} & & R^2 & & & R^3 & & & \\ & & | & & & | & & & \\ R^1 & — & N & = & C & — & B & — & C=N—R^4 \end{array}$$

wherein R^1, R^2, R^3, and R^4 can each be selected from H, substituted alkyl and aryl groups such that each R^1-N=C-R^2 and R^3-C=N-R^4 form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S. CR^5R^6, NR^7 and C=O, wherein R^5, R^6, and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl_2, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, Co(2,2-bispyridylamine)$_2O_2ClO_4$, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Other examples include Mn gluconate, $Mn(CF_3SO_3)_2$, $Co(NH_3)_5Cl$, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]\text{-}(ClO_4)_3$.

The bleach catalysts may also be prepared by combining a water-soluble ligand with a water-soluble manganese salt in aqueous media and concentrating the resulting mixture by evaporation. Any convenient water-soluble salt of manganese can be used herein. Manganese (II), (III), (IV) and/or (V) is readily available on a commercial scale. In some instances, sufficient manganese may be present in the wash liquor, but, in general, it is preferred to add Mn cations in the compositions used to ensure its presence in catalytically-effective amounts. Thus, the sodium salt of the ligand and a member selected from the group consisting of $MnSO_4$, $Mn(ClO_4)_2$ or $MnCl_2$ (least preferred) are dissolved in water at molar ratios of ligand:Mn salt in the range of about 1:4 to 4:1 at neutral or slightly alkaline pH. The water may first be de-oxygenated by boiling and cooled by spraying with nitrogen. The resulting solution is evaporated (under N_2, if desired) and the resulting solids are used in the bleaching and detergent compositions herein without further purification.

In an alternate mode, the water-soluble manganese source, such as $MnSO_4$, is added to the bleach/cleaning composition used or to the aqueous bleaching/cleaning bath which comprises the ligand. Some type of complex is apparently formed in situ, and improved bleach performance is secured. In such an in situ process, it is convenient to use a considerable molar excess of the ligand over the manganese, and mole ratios of ligand:Mn typically are 3:1 to 15:1. The additional ligand also serves to scavenge vagrant metal ions such as iron and copper,

thereby protecting the bleach from decomposition. One possible such system is described in European patent application, publication no. 549,271.

While the structures of the bleach-catalyzing manganese complexes useful in the present invention have not been elucidated, it may be speculated that they comprise chelates or other hydrated coordination complexes which result from the interaction of the carboxyl and nitrogen atoms of the ligand with the manganese cation. Likewise, the oxidation state of the manganese cation during the catalytic process is not known with certainty, and may be the (+II), (+III), (+IV) or (+V) valence state. Due to the ligands' possible six points of attachment to the manganese cation, it may be reasonably speculated that multi-nuclear species and/or "cage" structures may exist in the aqueous bleaching media. Whatever the form of the active Mn·ligand species which actually exists, it functions in an apparently catalytic manner to provide improved bleaching performances on stubborn stains such as tea, ketchup, coffee, wine, juice, and the like.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Preferred are cobalt (III) catalysts having the formula:

$$Co[(NH_3)_nM'_mB'_bT'_tQ_qP_p]\ Y_y$$

wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and $n + m + 2b + 3t + 4q + 5p = 6$; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, iodide, I_3^-, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^-, BF_4^-, $B(Ph)_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof [optionally, Y can be protonated if more than one anionic group exists in Y, e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, etc., and further, Y may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants, e.g.,

linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc., and/or anionic polymers, e.g., polyacrylates, polymethacrylates, etc.]; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts (preferably less than about 0.2 volts) versus a normal hydrogen electrode.

Preferred cobalt catalysts of this type have the formula:

$$[Co(NH_3)_n(M')_m]\ Y_y$$

wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); m+n = 6; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[Co(NH_3)_5Cl]\ Y_y$, and especially $[Co(NH_3)_5Cl]Cl_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\ T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 $M^{-1}\ s^{-1}$ (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I_3^-, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^-, BF_4^-, $B(Ph)_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, etc. Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F^-, SO_4^{-2}, NCS^-, SCN^-, $S_2O_3^{-2}$, NH_3, PO_4^{3-}, and carboxylates (which preferably are mono-carboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, $HOC(O)CH_2C(O)O$-, etc.) Preferred M moieties are substituted and unsubstituted C_1-C_{30} carboxylic acids having the formulas:

RC(O)O-

wherein R is preferably selected from the group consisting of hydrogen and C_1-C_{30} (preferably C_1-C_{18}) unsubstituted and substituted alkyl, C_6-C_{30} (preferably C_6-C_{18}) unsubstituted and substituted aryl, and C_3-C_{30} (preferably C_5-C_{18}) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of $-NR'_3$, $-NR'_4{}^+$, -C(O)OR', -OR', -C(O)NR'$_2$, wherein R' is selected from the group consisting of hydrogen and C_1-C_6 moieties. Such substituted R therefore include the moieties $-(CH_2)_nOH$ and $-(CH_2)_nNR'_4{}^+$, wherein n is an integer from 1 to about 16, preferably from about 2 to about 10, and most preferably from about 2 to about 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched C_4-C_{12} alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as k_{OH}) for cobalt pentaamine catalysts complexed with oxalate (k_{OH}= 2.5 x 10^{-4} M^{-1} s^{-1} (25°C)), NCS^- (k_{OH}= 5.0 x 10^{-4} M^{-1} s^{-1} (25°C)), formate (k_{OH}= 5.8 x 10^{-4} M^{-1} s^{-1} (25°C)), and acetate (k_{OH}= 9.6 x 10^{-4} M^{-1} s^{-1} (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]\ T_y$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$.

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article hereinbefore and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

These catalysts may be coprocessed with adjunct materials so as to reduce the color impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

As a practical matter, and not by way of limitation, the compositions used herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in an aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst by weight of the cleaning compositions.

4. pH and Buffering Variation

Many compositions used herein will be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art.

The preferred ADD compositions used herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. The pH-adjusting components are selected so that when the ADD is dissolved in water at a concentration of 1,000 - 10,000 ppm, the pH remains in the range of above about 8, preferably from about 9.5 to about 11. The preferred nonphosphate pH-adjusting component of the invention is selected from the group consisting of:

(i) sodium carbonate or sesquicarbonate;

(ii) sodium silicate, preferably hydrous sodium silicate having SiO_2:Na_2O ratio of from about 1:1 to about 2:1, and mixtures thereof with limited quantities of sodium metasilicate;

(iii) sodium citrate;
(iv) citric acid;
(v) sodium bicarbonate;
(vi) sodium borate, preferably borax;
(vii) sodium hydroxide; and
(viii) mixtures of (i)-(vii).

Preferred embodiments contain low levels of silicate (i.e. from about 3% to about 10% SiO_2).

Illustrative of highly preferred pH-adjusting component systems are binary mixtures of granular sodium citrate with anhydrous sodium carbonate, and three-component mixtures of granular sodium citrate trihydrate, citric acid monohydrate and anhydrous sodium carbonate.

The amount of the pH adjusting component in the compositions used herein is preferably from about 1% to about 50%, by weight of the composition. In a preferred embodiment, the pH-adjusting component is present in the composition used herein in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.

For compositions used herein having a pH between about 9.5 and about 11 of the initial wash solution, particularly preferred ADD embodiments used herein comprise, by weight of ADD, from about 5% to about 40%, preferably from about 10% to about 30%, most preferably from about 15% to about 20%, of sodium citrate with from about 5% to about 30%, preferably from about 7% to 25%, most preferably from about 8% to about 20% sodium carbonate.

The essential pH-adjusting system can be complemented (i.e. for improved sequestration in hard water) by other optional detergency builder salts selected from nonphosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, non-phosphorus organic builders can be used for their sequestering properties. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid; nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethoxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts.

(a) Water-Soluble Silicates

The compositions used herein may further comprise water-soluble silicates. Water-soluble silicates herein are any silicates which are soluble to the extent that they do not adversely affect spotting/filming characteristics of the ADD composition.

Examples of silicates are sodium metasilicate and, more generally, the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1; and layered

silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6® is a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, Na SKS-6 and other water-soluble silicates useful herein do not contain aluminum. NaSKS-6 is the δ-Na_2SiO_5 form of layered silicate and can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1} \cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the α-, β- and γ- forms. Other silicates may also be useful, such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Silicates particularly useful in (ADD) compositions used herein include granular hydrous 2-ratio silicates such as BRITESIL® H20 from PQ Corp., and the commonly sourced BRITESIL® H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

6. Chelating Agents

The compositions used herein may also optionally contain one or more transition-metal selective sequestrants, "chelants" or "chelating agents", e.g., iron and/or copper and/or manganese chelating agents. Chelating agents suitable for use herein can be selected from the group consisting of aminocarboxylates, phosphonates (especially the aminophosphonates), polyfunctionally-substituted aromatic chelating agents, and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to control iron, copper and manganese in washing solutions which are known to decompose hydrogen peroxide and/or bleach activators; other benefits include inorganic film prevention or scale inhibition. Commercial chelating agents for use herein include the DEQUEST® series, and chelants from Monsanto, DuPont, and Nalco, Inc.

Aminocarboxylates useful as optional chelating agents are further illustrated by ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof. In general, chelant mixtures may be used for a combination of functions, such as multiple transition-metal control, long-term product stabilization, and/or control of precipitated transition metal oxides and/or hydroxides.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A highly preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially (but not limited to) the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The trisodium salt is preferred though other forms, such as magnesium salts, may also be useful.

Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are acceptable in detergent compositions, and include the ethylenediaminetetrakis (methylenephosphonates) and the diethylenetriaminepentakis (methylene phosphonates). Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

If utilized, chelating agents or transition-metal-selective sequestrants will preferably comprise from about 0.001% to about 10%, more preferably from about 0.05% to about 1% by weight of the compositions used herein.

7. <u>Dispersant Polymer</u> - Preferred compositions used herein may additionally contain a dispersant polymer. When present, a dispersant polymer in the compositions used herein is typically at levels in the range from 0 to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 8% by weight of the composition used . Dispersant polymers are useful for improved filming performance of the present compositions used, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.5. Particularly preferred are polymers which inhibit the deposition of calcium carbonate or magnesium silicate on dishware.

Dispersant polymers suitable for use herein are further illustrated by the film-forming polymers described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983.

Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1,000 to about 500,000, more preferably is from about 1,000 to about 250,000, and most preferably, especially if the composition to be used is an ADD composition is for use in the method in a North American automatic dishwashing appliances, is from about 1,000 to about 5,000.

Other suitable dispersant polymers include those disclosed in U.S. Patent No. 3,308,067 issued March 7, 1967, to Diehl. Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid, maleic acid (or maleic anhydride), fumaric

acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence of monomeric segments containing no carboxylate radicals such as methyl vinyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 50% by weight of the dispersant polymer.

Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50%, preferably less than about 20%, by weight of the dispersant polymer can also be used. Most preferably, such dispersant polymer has a molecular weight of from about 4,000 to about 20,000 and an acrylamide content of from about 0% to about 15%, by weight of the polymer.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 20% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% by weight of a substituted acrylic monomer or its salt and have the general formula: $-[(C(R^2)C(R^1)(C(O)OR^3)]$ wherein the apparently unfilled valencies are in fact occupied by hydrogen and at least one of the substituents R^1, R^2, or R^3, preferably R^1 or R^2, is a 1 to 4 carbon alkyl or hydroxyalkyl group; R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R^1 is methyl, R^2 is hydrogen, and R^3 is sodium.

Suitable low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of about 3,500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766, and 5,084,535.

Agglomerated forms of the compositions used herein may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono-

and dicarboxylate monomers are disclosed in European Patent Application No. 66,915, published December 15, 1982.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan. Such compounds for example, having a melting point within the range of from about 30°C to about 100°C, can be obtained at molecular weights of 1,450, 3,400, 4,500, 6,000, 7,400, 9,500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula: $HO(CH_2CH_2O)_m(CH_2CH(CH_3)O)_n(CH(CH_3)CH_2O)_oOH$ wherein m, n, and o are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrins and starch hydrolysates described in U.S. Pat No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDonald, issued Feb. 27, 1979. Preferred cellulose-derived dispersant polymers are the carboxymethyl celluloses.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polyaspartate.

8. Material Care Agents - The compositions used herein may contain one or more material care agents which are effective as corrosion inhibitors and/or anti-tarnish aids. Such materials are preferred components of ADD compositions used herein especially in certain European countries where the use of electroplated nickel silver and sterling silver is still comparatively common in domestic flatware, or when aluminum protection is a concern and the composition is low in silicate. Generally, such material care agents include metasilicate, silicate, bismuth salts, manganese salts, paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminium fatty acid salts, and mixtures thereof.

When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the composition used. Suitable corrosion inhibitors include paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from about 20 to about 50; preferred paraffin oil is selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68. A paraffin oil meeting those characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70. Additionally, the addition of low levels of bismuth nitrate (i.e., $Bi(NO_3)_3$) is also preferred.

Other corrosion inhibitor compounds include benzotriazole and comparable compounds; mercaptans or thiols including thionaphtol and thioanthranol; and finely divided Aluminium fatty acid salts, such as aluminium tristearate. The formulator will recognize that such materials will generally be used judiciously and in limited quantities so as to avoid any tendency to produce spots or films on glassware or to compromise the bleaching action of the compositions. For this reason, mercaptan anti-tarnishes which are quite strongly bleach-reactive and common fatty carboxylic acids which precipitate with calcium in particular are preferably avoided.

9. Silicone and Phosphate Ester Suds Suppressors - The compositions used in the methods of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%. However, generally (for cost and/or deposition considerations) preferred compositions used herein do not comprise suds suppressors or comprise suds suppressors only at low levels, e.g., less than about 0.1% of active suds suppressing agent.

Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica and/or with surface-active nonsilicon components, as illustrated by a suds suppressor comprising 12% silicone/silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

If it is desired to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891, issued April 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred

alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the compositions used.

10. Other Optional Adjuncts - Depending on whether a greater or lesser degree of compactness is required, filler materials can also be present in the compositions used in the methods herein. These include sucrose, sucrose esters, sodium sulfate, potassium sulfate, etc., in amounts up to about 70%, preferably from 0% to about 40% of the ADD composition. Preferred filler is sodium sulfate, especially in good grades having at most low levels of trace impurities.

Sodium sulfate used herein preferably has a purity sufficient to ensure it is non-reactive with bleach; it may also be treated with low levels of sequestrants, such as phosphonates or EDDS in magnesium-salt form. Note that preferences, in terms of purity sufficient to avoid decomposing bleach, applies also to pH-adjusting component ingredients, specifically including any silicates used herein.

Although optionally present in the compositions used herein, the present invention encompasses embodiments which are substantially free from sodium chloride or potassium chloride.

Hydrotrope materials such as sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, etc., can be present, e.g., for better dispersing surfactant.

Bleach-stable perfumes (stable as to odor); and bleach-stable dyes such as those disclosed in U.S. Patent 4,714,562, Roselle et al, issued December 22, 1987 can also be added to the present compositions in appropriate amounts. Other common detergent ingredients consistent with the spirit and scope of the present invention are not excluded.

Since compositions used herein, especially the ADD compositions used herein, can contain water-sensitive ingredients or ingredients which can co-react when brought together in an aqueous environment, it is desirable to keep the free moisture content of the compositions used at a minimum, e.g., 7% or less, preferably 4% or less of the composition; and to provide packaging which is substantially impermeable to water and carbon dioxide. Coating measures have been described herein to illustrate a way to protect the ingredients from each other and from air and moisture. Plastic bottles, including refillable or recyclable types, as well as conventional barrier cartons or boxes are another helpful means of assuring maximum shelf-storage stability. As noted, when ingredients are not highly compatible, it may further be desirable to coat at least one such ingredient with a low-foaming nonionic surfactant for

protection. There are numerous waxy materials which can readily be used to form suitable coated particles of any such otherwise incompatible components; however, the formulator prefers those materials which do not have a marked tendency to deposit or form films on dishes including those of plastic construction.

Some preferred substantially chlorine bleach-free granular automatic dishwashing compositions for use in the methods of the invention are as follows: a substantially chlorine-bleach free automatic dishwashing composition comprising amylase (e.g., TERMAMYL®) and/or a bleach stable amylase and a bleach system comprising a source of hydrogen peroxide selected from sodium perborate and sodium percarbonate and a cobalt catalyst as defined herein.

There is also contemplated a substantially chlorine-bleach free automatic dishwashing composition comprising an oxidative stability-enhanced amylase and a bleach system comprising a source of hydrogen peroxide selected from sodium perborate and sodium percarbonate, a cobalt catalyst, and TAED or NOBS.

The following nonlimiting examples further illustrate compositions suitable for use in the methods of the present invention.

EXAMPLE 1

Automatic dishwashing compositions:

Ingredients:	Weight%	
	A	B
Sodium Tripolyphosphate (STPP)	24.0	45
Sodium carbonate	20.0	13.5
Hydrated 2.0r silicate	15	13.5
Poly-Tergent® SLF-18B Nonionic surfactant[4]	2.0	2.0
C_{13} Amine Oxide	1.0	1.0
Polymer[1]	4.0	--
Protease (4% active)	0.83	0.83
Amylase (0.8% active)	0.5	0.5
Perborate monohydrate (15.5% Active AvO)[2]	14.5	14.5
Cobalt catalyst[3]	0.008	--
Dibenzoyl Peroxide (18% active)	4.4	4.4
Water, sodium sulfate and misc.	Balance	Balance

[1] Terpolymer selected from either 60% acrylic acid/20% maleic acid/20% ethyl acrylate, or 70% acrylic acid/10% maleic acid/20% ethyl acrylate.

2 The AvO level of the above formula is 2.2%.

3 Pentaammineacetatocobalt(III) nitrate prepared as described hereinbefore; may be replaced by MnTACN.

4 Epoxy-capped poly(oxyalkylated) alcohol of Example III of WO 94/22800 wherein 1,2-epoxydodecane is substituted for 1,2-epoxydecane.

The following examples further illustrate phosphate built ADD compositions which contain a bleach/enzyme particle, but are not intended to be limiting thereof. These compositions are suitable for use in the methods of the present invention. All percentages noted are by weight of the finished compositions, other than the perborate (monohydrate) component, which is listed as AvO.

EXAMPLES 2 - 3

	2	3
Catalyst[1]	0.008	0.004
Savinase™ 12T	--	1.1
Protease D	0.9	--
Duramyl™	1.5	0.75
STPP	31.0	30.0
Na_2CO_3	20.0	30.5
Polymer[2]	4.0	--
Perborate (AvO)	2.2	0.7
Dibenzoyl Peroxide	0.2	0.15
2 R Silicate (SiO_2)	8.0	3.5
Paraffin	0.5	0.5
Benzotriazole	0.3	0.15
SLF-18 Nonionic surfactant[3]	1.0	1.0
C_{13} Amine Oxide	1.0	1.0
Sodium Sulfate, Moisture	---------Balance---------	

1 Pentaammineacetatocobalt (III) nitrate; may be replaced by MnTACN.

2 Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers.

3 Supplied by Olin Corporation (cloud point=18°C).

4 An alkyl carboxy ethoxylate having an average of C_{13} alkyl and 6.5 ethoxylates.

In Compositions of Examples 2 and 3, respectively, the catalyst and enzymes are introduced into the compositions as 200-2400 micron composite particles which are prepared by spray coating, fluidized bed granulation, marumarizing, prilling or flaking/grinding operations. If desired, the protease and amylase enzymes may be separately formed into their respective

catalyst/enzyme composite particles, for reasons of stability, and these separate composites added to the compositions.

EXAMPLES 4 - 5

The following describes catalyst/enzyme particles (prepared by drum granulation) for use in the present invention compositions. For example 5, the catalyst is incorporated as part of the granule core, and for example 4 the catalyst is post added as a coating. The mean particle size is in the range from about 200 to 800 microns.

Catalyst/Enzyme Particles for Examples 4 and 5

	4	5
Core		
Cobalt Catalyst (PAC)	-	0.3
Amylase, commercial	0.4	0.4
Fibrous Cellulose	2.0	2.0
PVP	1.0	1.0
Sodium Sulphate	93.3	93.3
Coating		
Titanium Dioxide	2.0	2.0
PEG	1.0	1.0
Cobalt Catalyst (PAC)	0.3	-

Granular dishwashing detergents wherein Example 4 is a Compact product and Example 5 is a Regular/Fluffy product are as follows:

	4	5
Composite Particle	1.5	0.75
Savinase™ 12T	2.2	-
Protease D	--	0.45
STPP	34.5	30.0
Na_2CO_3	20.0	30.5
Acusol 480N	4.0	--
Perborate(AvO)	2.2	0.7
Dibenzoyl Peroxide	0.2	0.15
2 R Silicate(SiO_2)	8.0	3.5
Paraffin	--	0.5
Benzotriazole	--	0.15
SLF-18 Nonionic surfactant	2.0	2.0
Tergitol 15S9 Nonionic surfactant	1.0	1.0

C_{13} Amine Oxide	0.05	1.0
Sodium Sulphate, Moisture	---to balance-----	

Other compositions herein are as follows:

EXAMPLES 6 - 9

	6	7	8	9
STPP	34.4	34.4	34.4	34.4
Na_2CO_3	20.0	30.0	30.5	30.5
Polymer[3]	4.0	--	--	2.0
Perborate (AvO)	2.2	1.0	0.7	1.5
Catalyst[1]	0.008	0.004	0.004	0.005
Savinase™ 6.0T	--	2.0[2]	2.0[2]	
Protease D	0.9	--	--	0.05
Duramyl™	1.5	0.75	--	0.05
Termamyl™ 6.0T	--	--	1.0	0.02
Dibenzoyl Peroxide (active)	0.8	0.6	0.4	--
2 R Silicate (SiO_2)	8.0	6.0	4.0	5.0
SLF-18 Nonionic Surfactant	2.0	1.5	1.2	1.3
C_{12} phosphine oxide	0.5	--	1.0	--
C_{12} sulfoxide	--	0.5	--	1.0
Sodium Sulfate, Moisture	------------- Balance ------------------------------			

[1] Pentaamineacetatocobalt (III) nitrate; may be replaced by MnTACN.

[2] May be replaced by 0.45 Protease D.

[3] Polyacrylate or Acusol 480N.

In Compositions of Examples 6-8, respectively, the catalyst and enzymes are introduced into the final compositions as 200-2400 micron catalyst/enzyme composite particles which are prepared by spray coating, marumarizing, prilling or flaking/grinding operations. If desired, the protease and amylase enzymes may be separately formed into their respective catalyst/enzyme composite particles, for reasons of stability, and these separate composites added to the compositions.

EXAMPLES 10 - 12

	10	11	12
STPP	31.0	31.0	31.0
Na_2CO_3	20.0	20.0	20.0
Polymer[3]	4.0	4.0	4.0
Perborate (AvO)	2.2	2.2	2.2
Catalyst[1]	0.008	--	0.018

Savinase™ 6.0T[2]	2.0	2.0	2.0
Termamyl™ 6.0T	1.0	1.0	1.0
TAED	2.0	--	1.0
Cationic Activator[4]	--	2.0	--
2 R Silicate (SiO_2)	8.0	8.0	8.0
Metasilicate	--	--	2.5
$C_{16/18}$ Amine Oxide	0.25	0.25	0.75
SLF-18 Nonionic surf.	0.5	1.0	1.5
Tergitol 15S9 Nonionic surf.	1.0	1.0	0.75
Sodium Sulfate, Moisture	------------- Balance --------------		

[1]Pentaamineacetatocobalt (III) nitrate; may be replaced by MnTACN.

[2] May be replaced by 0.45 Protease D.

[3] Polyacrylate or Acusol 480N.

[4] 6-Trimethylammoniocaproyl caprolactam, tosylate salt.

Example 13

Method of the present invention

Any of the foregoing ADD compositions can be used in the conventional manner in an automatic dishwashing machine to cleanse plasticware, dishware, glassware, cooking/eating utensils, and the like.

What is claimed is:

1. A method for removing stains from a surface and preventing the redeposition of soil from a surface comprising the steps of applying an aqueous solution of a composition to a stained surface in need of stain removal, wherein said composition comprises:

(a) from 0.1% to 15%, by weight of the composition of an oxide surfactant, said oxide surfactant being selected from the group consisting of, amine oxides, phosphine oxides, sulfoxides and mixtures thereof;

(b) from 0.1% to 15%, by weight of the composition of one or more low cloud point nonionic surfactants having a cloud point of less than 30°C, said nonionic surfactants are selected from the group consisting of ethoxylated-propoxylated alcohol, capped poly(oxyalkylated) alcohols and mixtures thereof; wherein said capped nonionic surfactant is substantially free of dimers and trimers;

(c) optionally, from 0.1% to 40% by weight of the composition of a bleaching agent;

(d) optionally, from 5% to 90%, by weight of the composition of a builder; and

(e) adjunct materials;

wherein the weight ratio of said nonionic surfactant to said oxide surfactant being within the range of from 25:1 to 1:5, preferably 3:1 to 15:1; said stained surface is a hydrophobic surface; said stains are selected from the group consisting of tomato stains, carotene stains, and mixtures thereof; and wherein said composition prevents redeposition of said stains once it has been removed from said stained surface.

2. The method according to Claim 1 wherein said composition further comprises a detersive enzyme.

3. The method according to either of Claims 1 or 2 wherein said composition further comprises a metal-containing bleach catalyst selected from manganese-containing bleach catalysts, cobalt-containing bleach catalysts, and mixtures thereof.

4. The method according to any of Claims 1 to 3 wherein the composition comprises a n oxygen bleaching agent.

5. The method according to any of Claims 1-4 wherein the low cloud point nonionic surfactant further has a hydrophile-lipophile balance value within the range of from 1 to 10, preferably from 3 to 8.

6. The method according to any of Claims 1-5 wherein the low cloud point nonionic surfactants have a cloud point of less than 20°C.

7. The method according to any of Claims 1-6 further comprising a high cloud point nonionic surfactant having a cloud point of greater than 30°C.

8. The method according to any of Claims 1-7 wherein said oxide surfactant is an amine oxide surfactant having the formula:

$$R^3(OR^4)_x\overset{\displaystyle O}{\overset{|}{N}}(R^5)_2$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from 8 to 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms or mixtures thereof; x is from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3 carbon atoms or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups.

9. The method according to any of Claims 1 to 8, wherein said composition is an automatic dishwashing composition.

10. The method according to any of Claims 1 to 9 comprising less than 0.1% of active suds suppressing agent.

11. The method according to any of Claims 1-10 wherein said surface is selected from the group consisting of tableware, fixed internal surfaces of an automatic dishwasher, removable internal surfaces of an automatic dishwasher and mixtures thereof.

12. The method according to any of Claims 1-11 wherein said amine oxide has the formula:

$$CH_3(CH_2)_{15}\overset{\displaystyle O}{\overset{|}{N}}(R^5)_2$$

wherein R^5 is as herein before defined.